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(54) **Method of preparing modified starch granules.**

(57) Disclosed is a method of producing starch granules having modified characteristics, by treating starch granules with an amylase. Where cereal starch granules are lightly decomposed with α -amylase, the viscosity characteristic of them greatly varies so that the viscosity of the decomposed granules decreases to such a degree that they are only slightly viscous. The decomposed starch granules may be used in preparing instant liquid foods, and the use of them is expected to be extremely broad. By appropriately blending the decomposed starch granules and other non-treated starch granules or decomposed starch granules, blends of different starch granules having various viscosity values can be obtained. Since the paste or liquid to be prepared from the enzyme-treated starch granules is smooth and soft to the touch, they may be expected to be useful as base materials for producing various foods. Starch granules with holes may adsorb aromatic components. By combining them with enzyme-treated low-viscosity starch granules, various foods can be produced. Since the enzyme-treated low-viscosity starch granules of the invention may be produced extremely simply, they are useful as a raw material in the starch sugar industry.

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The present invention relates to a method of preparing starch granules having modified characteristics. More precisely, it relates to a method of preparing modified starch granules, in which starch granules are treated with various amylases to modify the characteristics of them.

5 BACKGROUND OF THE INVENTION

For improving and modifying physical properties of starch, heretofore, there is known a method of adding an α -amylase or acid to starch, when starch is blended with water for gelatinization, so as to lower the viscosity of the blend; or a method of adding various substances of a metal ion, an algal polysaccharide
10 or a water-soluble gum to starch so as to elevate or lower the physical properties of the starch gel. For modifying the characteristics of starch granules, there is known a method of crosslinking starch granules to make them low soluble.

However, a method has heretofore been unknown, in which starch granules are directly treated with an enzyme to modify the characteristics of the granules, whereby the physical properties of them are
15 noticeably varied when dissolved in water. Under the situation, the matter how greatly the physical properties of starch granules would vary in dissolution of them, when they are treated with an enzyme of what kind, is quite unknown at all, and the fact that the physical properties of starch granules would be varied greatly by such treatment has not heretofore been anticipated at all.

20 SUMMARY OF THE INVENTION

The present inventors variously investigated so as to modify the characteristics of starch granules by directly treating them with an enzyme and, as a result, have found that the intended object can be attained by treating starch granules with an amylase.

Specifically, after they treated starch granules with various amylases such as α -amylase, β -amylase or glucoamylase, took out the enzyme-treated starch granules and investigated the physical properties of them, they have found that the enzyme-treated starch granules display various physical properties when dissolved, depending upon the kind of the enzyme used for treatment and the kind of the starch granules to be treated therewith. On the basis of the finding, they have completed the present invention.

Accordingly, the present invention relates to a method of preparing starch granules with modified characteristics, in which starch granules are treated with an amylase.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows photographs of α -amylase-treated rice starch granules "Wakaho-no-minori", as taken with a scanning electromicroscope; in which A is a control sample (decomposition percentage, 0 %), B is a sample with a decomposition percentage of 2.0 %, and C is a sample with a decomposition percentage of 5.0 %.

Fig. 2 shows a viscograph of α -amylase-treated rice starch granules "Nihon-bare", in which A is a control sample (decomposition percentage, 0 %), B is a sample with a decomposition percentage of 0.5 %, C is a sample with a decomposition percentage of 0.9 %, D is a sample with a decomposition percentage of 1.9 %, and E is a sample with a decomposition percentage of 3.1 %.

DETAILED DESCRIPTION OF THE INVENTION

45 In the present invention, any starch granules from various sources may be used, such as those from rice, wheat, corn, potato and sweet potato.

As amylases for decomposition of such starch granules in accordance with the present invention, any one derived from various sources can be used. Generally used are commercial products, such as a purified
50 α -amylase (produced by Sigma Co., derived from *Bacillus amyloliquefaciens*, with 930 IU(international unit)/mg), a purified glucoamylase (produced by Seikagaku KK, derived from *Rhizopus niveus*, with 32.6 IU/mg), and a purified β -amylase (produced by Sigma Co., derived from TYPE1-B sweet potato, with 965 IU/mg). In treatment of starch granules with the enzyme, where the pH variation in the reaction system is small, use of any particular buffer would be unnecessary. As the case may be, usable are various buffers
55 such as a phosphoric acid buffer(pH 6.9), an acetic acid buffer (pH 5.2), and an acetic acid buffer (pH 4.8).

The enzymatic treatment of starch granules is to be effected in such a way that the starch granules are not over-decomposed. In general, it is effected in the manner that starch granules are decomposed to have a decomposition percentage of from 0.1 to 15.0 %. The concentration of the starch granules which are the

Table 1

Enzyme Decomposition Conditions of Rice Starch Grains					
Name of Enzyme	Determined Decomposition Percentage(%)	Amount of Starch(g)	Amount of Enzyme(mg)	Amount of Buffer(ml)	Decomposition Time(hr)
α - amylase	0.5	25	0.01	100	0.5~2.5
	1.0	25	0.10	100	1.0
	2.0	25	1.00	100	1.0~3.5
	3.0	25	5.00	100	2.0~4.0
	5.0	25	5.00	100	2.0~4.0
	0.5	25	1.00	100	1.0~5.5
glucoamylase	2.0	25	1.00	100	1.0~5.5
	2.5	25	2.00	100	2.0~8.0
	5.0	25	2.0	100	2.0~8.0
	30.0	25	10ml	100	9.
	0.4	10	0.01	50	4.
β - amylase	0.8	10	1ml	25	4

(*) Industrial crude enzyme liquid was used.

The difference in the enzyme decomposability with α - amylase between rice starch granules of different kinds was investigated with respect to the time - dependent variation thereof in a low decomposition percentage range (1 to 9 %) and in a high decomposition percentage range (8 to 27 %) to give a result that the enzyme decomposability of "Mochihikari" was high and that of "Nihon - bare" was low in both the low decomposition percentage range and the high decomposition percentage range. Regarding the difference in the decomposability between the other kinds, "Wakaho - no - megumi" and "Wakaho - no - minori" had the highest decomposability, then "Koshihikari" in this order, in the low decomposition percentage range, while there was almost no difference between "Wakaho - no - megumi" and "Wakaho - no - minori" in this respect. In the high decomposition range, "Wakaho - no - megumi" had the highest decomposability, then "Wakaho - no - minori" and then "Koshihikari" in this order, but the difference between them was not so large.

With respect to glucoamylase, there was almost no difference in the decomposability between rice starch granules of different kinds.

With respect to β - amylase, a large amount of concentrated pure enzyme liquid thereof was added to the reaction system but the enzyme decomposability thereof of decomposing rice starch grains was weak.

In every enzyme tested, there was admitted no relationship between the protein and amylose content therein and the enzyme decomposability.

Rice starch granules as decomposed by α - amylase in a decomposition percentage of 0 %, 2 % and 5 % were observed by SEM, and the photographs taken are shown in Fig. 1.

The outward appearance of the rice starch grains as decomposed with the enzyme in a decomposition percentage of 1 to 2 % was not specifically different from that of the non - treated rice starch granules. However, the rice starch grains as decomposed with it in a decomposition percentage of 5 % gave definite holes. With elevation of the decomposition percentage, the number of the holes on the surface of the decomposed starch granules and the size of them increased. The starch granules were admitted to be destroyed in a decomposition percentage of 20 %; and a fairly large number of starch granules were destroyed in a decomposition percentage of 25 %.

Also in the case of glucoamylase, the number of the holes and the size of them on the surface of the decomposed starch granules increased with elevation of the decomposition percentage. However, when glucoamylase was compared with α - amylase with respect to the decomposability in the same decomposition percentage, the size of the holes as made with glucoamylase was smaller than that with α - amylase. Even in the decomposition percentage of 30 %, the number of the holes and the size of them increased with glucoamylase, but the shape of the decomposed starch granules was not destroyed but was maintained as it was.

However, decomposition with β - amylase was weak, and both the number of the holes and the size of them made in rice starch granules of all the kinds as decomposed with it were small.

Table 2 - Viscographic Characteristic Values of α -amylase-decomposed Starch Granules

Kind	Decomposition Percentage(%)	Gelatinization Temperature(°C)	Maximum Viscosity (g · cm)	Maximum Viscosity Temperature (°C)	Minimum Viscosity (g · cm)	Minimum Viscosity Temperature (°C)	Break-down Viscosity (g · cm)	Final Viscosity (g · cm)	Consistency (g · cm)	Set-back (g · cm)
Corn	0.0	78.0	10.0	89.0	5.1	95.0	4.9	19.4	14.3	8.3
	0.6	70.0	9.9	83.5	5.4	94.0	4.5	22.4	17.0	5.9
	1.1	69.0	9.4	80.5	4.5	93.5	4.9	21.0	16.5	6.2
	2.0	69.0	5.9	73.0	0.5	95.5	5.4	4.6	4.1	1.5
	3.3	69.0	5.6	73.0	0.3	95.0	5.3	4.0	3.7	1.3
	4.3	68.5	5.1	73.0	0.2	95.0	4.9	3.0	2.8	1.0
	7.2	68.5	5.2	73.0	0.0	94.5	5.2	5.6	5.6	1.3
	9.4	67.0	1.7	71.0	0.0	95.0	1.7	0.3	0.3	0.2
	14.0	65.0	0.4	69.0	0.0	96.0	0.4	0.1	0.1	0.0
Potato	0.0	61.0	35.0	67.5	7.5	96.0	27.5	19.0	11.5	2.5
	0.5	56.0	27.5	63.5	3.0	93.0	24.5	8.5	5.5	1.0
	0.9	54.0	27.5	64.0	3.0	94.0	24.5	8.5	5.5	0.5
	1.3	56.0	22.5	45.0	3.0	94.0	19.5	12.5	9.5	1.5
	2.0	56.0	8.5	11.9	0.0	96.0	8.5	0.2	0.2	0.2
	2.7	55.0	3.8	58.5	0.0	95.0	3.8	0.1	0.1	0.1
Wheat	0.0	74.0	9.4	89.0	3.6	95.0	5.8	24.0	20.4	7.9
	0.5	73.0	3.9	86.5	0.8	95.5	3.1	23.5	22.7	4.0
	0.9	76.0	3.1	86.0	0.3	95.5	2.8	21.0	20.7	2.5
	2.2	70.0	2.7	84.5	0.2	95.0	2.5	13.5	13.3	2.0
	3.0	69.0	1.8	83.5	0.1	95.0	1.7	9.3	9.2	0.9
	5.6	68.5	1.8	83.0	0.1	95.0	1.7	7.6	7.5	0.8
	7.4	68.0	1.4	81.0	0.1	95.0	1.3	6.2	6.1	0.5

The decomposability with glucoamylase and β -amylase was low. Particularly, they were decomposed only slightly with β -amylase.

The thus enzyme-decomposed four kinds of starch granules were observed by SEM. As a result, it was admitted that all the four kinds of starch granules were decomposed with α -amylase with increase of the number of the holes and the size of them along with elevation of the decomposition percentage. In addition, decomposition of corn starch granules with glucoamylase and β -amylase was also admitted.

Table 3 - Viscographic Characteristic Values of α -amylase-decomposed Rice Starch Granules

Variety	Decomposition Percentage(%)	Gelatinization Temperature(°C)	Maximum Viscosity (g·cm)	Maximum Temperature (°C)	Minimum Viscosity (g·cm)	Minimum Viscosity Temperature (°C)	Break-down (g·cm)	Final Viscosity (g·cm)	Consistency (g·cm)	Set-back (g·cm)
Makaho-no-megumi	0.0	70.0	8.2	87.5	4.1	96.0	4.1	10.5	6.4	4.4
	0.5	71.0	5.6	88.0	1.9	95.0	3.7	8.5	6.6	4.3
	0.9	71.0	4.9	89.5	1.8	96.0	3.1	7.4	5.6	3.8
	2.2	68.0	0.6	71.0	0.0	95.0	0.6	0.0	0.0	0.0
	3.2	N.D	N.D	N.D	0.0	94.0	N.D	1.2	1.2	0.6
Makaho-no-minori	5.0	67.0	0.1	70.0	0.0	95.0	0.1	0.0	0.0	0.0
	0.0	70.0	9.0	89.0	5.3	95.5	3.7	10.5	5.2	3.7
	0.5	72.0	4.8	87.0	1.2	96.0	3.6	7.1	5.9	3.8
	1.1	67.0	3.0	83.5	0.2	95.5	2.8	1.5	1.3	0.2
	2.2	57.5	1.1	74.5	0.0	95.5	1.1	0.5	0.5	0.1
Nihonbare	2.7	67.0	0.4	70.0	0.0	96.0	0.4	0.1	0.0	0.1
	4.5	66.0	0.3	69.0	0.0	94.5	0.3	0.1	0.1	0.1
	0.0	71.0	10.8	87.0	3.5	95.5	7.3	8.0	4.5	2.8
	0.5	68.0	5.8	84.0	0.6	96.0	5.2	3.4	2.8	1.8
	0.9	68.0	2.9	78.0	0.0	95.0	2.9	1.0	1.0	0.6
Koshihikar	1.9	67.5	0.8	73.0	0.0	96.0	0.8	0.0	0.0	0.1
	3.1	67.0	0.6	72.5	0.0	96.0	0.8	0.1	0.1	0.1
	5.1	N.D	N.D	N.D	0.0	94.5	N.D	N.D	N.D	N.D
	0.0	70.0	9.3	90.0	5.7	96.0	3.6	11.0	5.3	4.0
	0.4	69.0	6.6	87.5	1.5	95.5	5.1	5.8	4.3	2.5
Michihikar	1.1	65.5	2.0	76.5	0.0	94.5	2.0	0.8	0.8	0.6
	1.9	66.0	0.9	70.0	0.0	95.0	0.9	0.1	0.1	0.0
	2.9	67.0	0.4	70.0	0.0	95.0	0.4	0.2	0.2	0.1
	5.2	N.D	N.D	N.D	0.0	94.5	N.D	0.1	0.1	0.1
	0.0	60.5	6.9	67.0	3.6	94.5	3.3	6.8	3.2	1.4
	0.5	62.0	4.4	66.0	0.1	95.5	4.3	1.4	1.3	0.7
	1.0	63.5	1.1	65.5	0.0	93.0	1.1	0.2	0.2	0.2
	2.0	52.0	0.2	66.0	0.0	96.0	0.2	0.2	0.2	0.1
	3.0	N.D	N.D	N.D	0.0	96.0	N.D	0.2	0.2	0.1
	5.6	N.D	N.D	N.D	0.0	95.0	N.D	0.0	0.2	0.0

EXAMPLE 3

Enzyme-treated dry starch granules were obtained in the same manner as in Example 2, except that from 1 to 2 mg of glucoamylase of a commercial product and acetate acid buffer (200 mM, pH 5.2) were used. By observation with SEM, definite holes were found in the decomposed product with a decomposition

Table 4 - Viscometric Characteristic Values of Glucoamylase-decomposed Rice Starch Granules

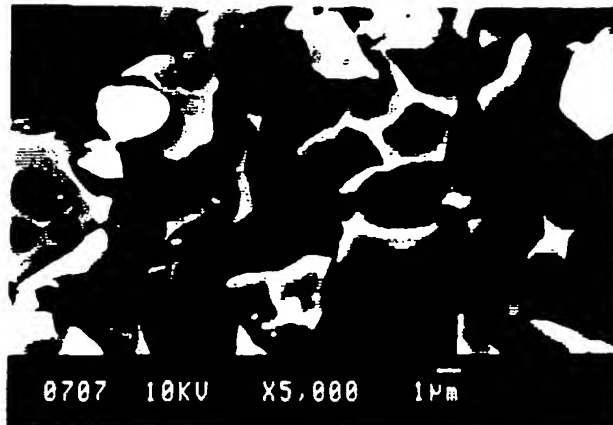
Variety	Decomposition Percentage(%)	Celatinization Temperature(°C)	Maximum Viscosity (g·cm)	Maximum Temperature (°C)	Minimum Viscosity (g·cm)	Minimum Temperature (°C)	Break-down	Final Viscosity (g·cm)	Consistency (g·cm)	Set-back (g·cm)
Wakaho-no-megumi	0.0	70.0	8.2	87.5	4.1	96.0	4.1	10.5	6.4	4.4
	0.5	74.0	8.3	89.0	5.1	96.0	3.2	10.2	5.1	3.9
	2.5	74.0	6.9	90.5	4.1	96.0	2.8	9.6	5.5	4.2
	5.2	75.0	7.0	89.0	4.3	95.0	2.7	10.2	5.9	4.2
Wakaho-no-minori	30.8	85.0	7.0	92.0	4.2	96.0	2.8	8.1	3.9	2.6
	0.0	70.0	9.0	89.0	5.3	95.5	3.7	10.5	5.2	3.7
	4.9	70.0	9.1	90.0	5.4	96.0	3.7	11.3	5.9	4.2
	0.0	71.0	10.8	87.0	3.5	95.5	7.3	8.0	4.5	2.8
Nihonbare	7.2	80.0	8.4	92.0	3.4	95.0	5.0	8.4	5.0	3.6
	0.0	70.0	9.3	90.0	5.7	96.0	3.6	11.0	5.3	4.0
	0.5	78.0	8.2	89.0	3.6	94.0	4.6	8.5	5.0	3.2
	6.0	79.5	8.4	91.0	3.6	95.0	4.8	8.6	5.0	3.5
Michihikar	0.0	60.5	6.9	67.0	3.6	94.5	3.3	6.8	3.2	1.4
	6.2	60.0	6.7	65.0	3.3	94.0	3.4	6.0	2.7	2.2

(*) Industrial crude enzyme liquid was used.

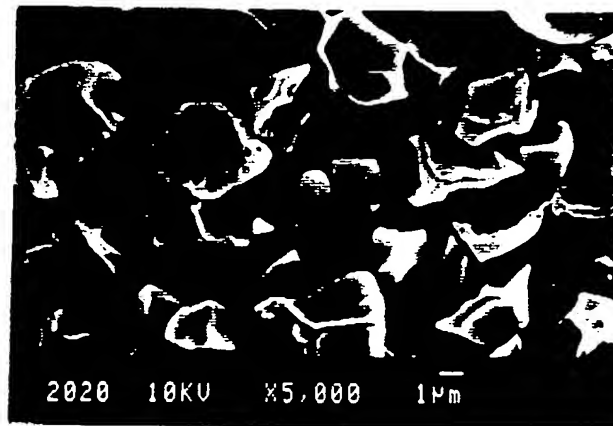
EXAMPLE 4

Corn starch granules were treated and decomposed with α -amylase in a decomposition percentage of from 0.5 to 1.0 % to obtain decomposed starch granules having a larger final viscosity and a larger

A



B



C

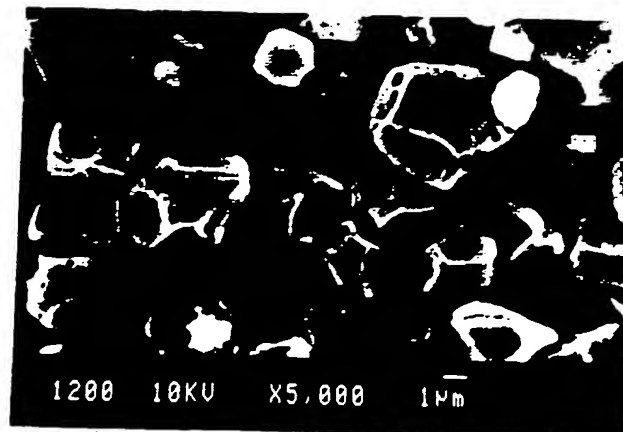
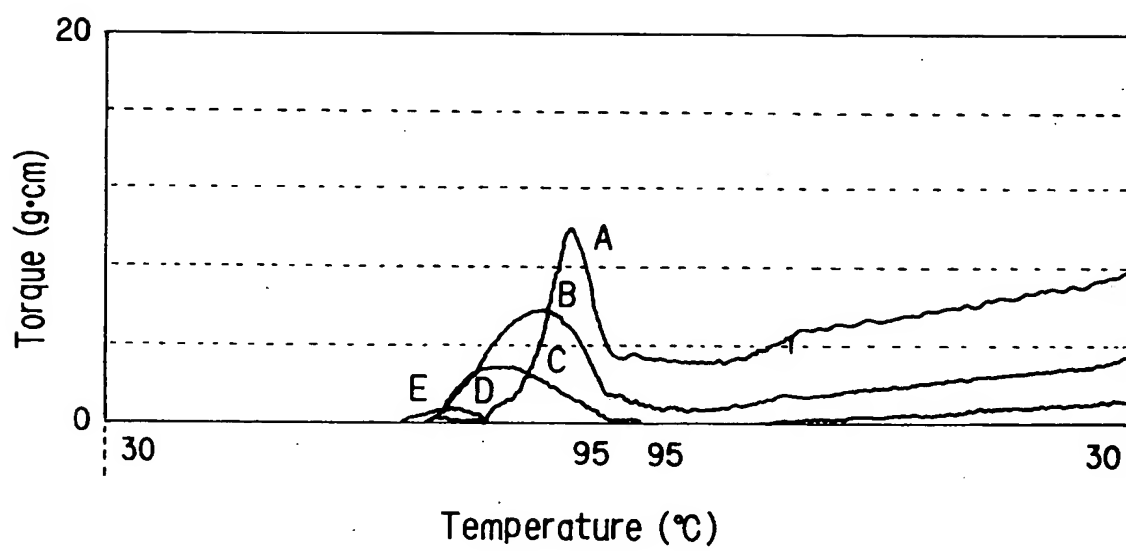


FIG. 2



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 11 8304

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	STARKE vol. 30, no. 6, 1978, WEINHEIM DE pages 186 - 191 H. FUWA, Y. SUGIMOTO, M. TANAKA, AND D. V. GLOVER 'susceptibility of various starch granules to amylases as seen by scanning electron microscope' * the whole paper *	1-3,5	C12P19/14 C12P19/20 //A23L1/00
X	EP-A-0 182 296 (CPC INTERNATIONAL INC.) * page 3, last paragraph - page 5 last paragraph *	1,2,5	
Y	* claims 1-5,9,10 *		
Y	idem.	4	
X	WO-A-8 904 842 (R.L. WHISTLER) * page 3, line 16 - page 4, line 7 *	1-3,5	
Y	* page 7, line 6 - line 25 *		
Y	* examples *		
Y	idem.	4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08B C12P
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 JANUARY 1993	Examiner BETTELS B.R.
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